

WHAT IS CLAIMED IS:

1. A biocidal composition comprising composite particles, each of said composite particles containing a shell and a core, said core comprising a metal or a metal-containing compound wherein the metal is a moiety selected from the group consisting of zinc, copper, bismuth, silver, zirconium, and combinations thereof, and said shell comprising a pyrrhione adduct comprising the reaction product of pyrrhione with a portion of said core metal or metal compound.

2. The composition of claim 1 wherein said core comprises surface oxidized copper powder or a copper-containing compound selected from the group consisting of cuprous oxide, copper hydroxide, copper containing salt(s), and combinations thereof.

3. The composition of claim 1 which is produced by reacting a copper compound selected from the group consisting of cuprous sulfide, copper thiocyanate, and combinations thereof, with a pyrrhione compound selected from the group consisting of pyrrhione acid, ammonium pyrrhione, tert-butylamine pyrrhione, calcium pyrrhione, dithiobis (pyridine-N-oxide), a magnesium salt adduct of dithiobis (pyridine-N-oxide) and combinations thereof, and sodium pyrrhione, potassium pyrrhione, lithium pyrrhione, and combinations thereof, to cause transchelation of said pyrrhione compound to copper pyrrhione.

4. The composition of claim 2 wherein said copper-powder or copper containing compound is present in said composition in an amount of from about 99 to about 60% by weight, based upon the total weight of said composition.

5. The composition of claim 3 wherein said copper-containing composite is present in said composition in an amount of from about 98 to about 80% by weight, based upon the total weight of said composition.

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6. The composition of claim 4 wherein said copper-containing composite is present in said composition in an amount of from about 97 to about 86% by weight, based upon the total weight of said composition.

7. The composition of claim 2 wherein said copper pyrithione adduct shell is present in an amount of from about 1 to about 40% by weight, based upon the total weight of said composition.

8. The composition of claim 6 wherein said copper pyrithione adduct shell comprises from about 2 to about 20% by weight, based on the total weight of said composition.

9. The composition of claim 7 wherein said copper pyrithione adduct shell comprises from about 3 to about 14% by weight, based on the total weight of said composition.

10. The composition of claim 2, further comprising surfactant or a fatty acid coating on said particle of said copper-containing salt.

11. The composition of claim 10 wherein said fatty acid is selected from the group consisting of stearic, oleic, glycerol, and combinations thereof.

12. A method of making a composite particle of copper pyrithione and a copper-containing compound by reacting pyrithione acid, or a water-soluble salt of pyrithione selected from the group consisting of sodium pyrithione, lithium pyrithione, potassium pyrithione, dithiobis (pyridine-N-oxide), a magnesium salt adduct of dithiobis (pyridine-N-oxide), and combinations thereof, and with copper powder or a copper compound selected from the group consisting of low solubility copper salts or copper oxide, copper hydroxide, and combinations thereof.

13. A method of making a biocide composition by reacting a water-soluble pyrrithione salt with copper powder or a copper salt in order to cause transchelation of said pyrrithione salt, thereby forming composite particles comprising a core of said copper powder or copper salt and a shell of copper
5 pyrrithione.

112/2 14. The composition of claim 12 wherein said water-soluble pyrrithione salt has a water solubility greater than about 4 ppm.

15. The composition of claim 12 wherein said water-soluble pyrrithione salt is selected from the group consisting of pyrrithione acid, ammonium pyrrithione, tert-butylamine pyrrithione, calcium pyrrithione, dithiobis (pyridine-N-oxide), a magnesium salt adduct of dithiobis (pyridine-N-oxide) and combinations
5 thereof, and sodium pyrrithione, potassium pyrrithione, lithium pyrrithione, and combinations thereof, to cause transchelation of said pyrrithione compound to copper pyrrithione.

16. The composition of claim 12 wherein said copper salt is selected from the group consisting of cuprous sulfide, copper thiocyanate, and combinations thereof.

17. The composition of claim 12 wherein said copper powder or copper compound comprises from about 99 to about 60% by weight, based on the total weight of said composition.

18. The composition of claim 17 wherein said copper-containing compound comprises from about 98 to about 80% by weight, based on the total weight of said composition.

19. The composition of claim 18 wherein said copper-containing compound comprises from about 97 to about 86% by weight, based on the total weight of said composition.

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20. The composition of claim 12 wherein said copper pyrithione adduct comprises from about 1 to about 40% by weight, based on the total weight of said composition.

21. The composition of claim 20 wherein said copper pyrithione adduct comprises from about 2 to about 20% by weight, based on the total weight of said composition.

22. The composition of claim 21 wherein said copper pyrithione adduct comprises from about 3 to about 14% by weight, based on the total weight of said composition.

23. The composition of claim 12 further comprising the step of coating said particles with a surfactant or a fatty acid.

24. The composition of claim 23 wherein said fatty acid is selected from the group consisting of stearic, oleic, glycerol, and combinations thereof.

25. A coating composition, comprising:

(a) a base medium; and,

(b) an antifouling composition comprising composite particles comprising a shell and a core, said core comprising an antihard-fouling effective amount of copper-containing compound particles coated with said shell comprising an antisoft-fouling effective amount of copper pyrithione.

26. The coating composition of claim 25 wherein said antifouling composition further comprises a coating of a fatty acid selected from the group consisting of stearic, oleic, glycerol, and combinations thereof.

27. The coating composition of claim 25 wherein said copper-containing core compounds is selected from the group consisting of cuprous oxide, cuprous sulfide, copper thiocyanate, copper hydroxide, and combinations thereof.

28. The coating composition of claim 25 wherein said copper-containing core compounds comprises from about 99 to about 60% by weight, based on the total weight of said antifouling agent.

29. The antifouling composition of claim 25 wherein said copper pyrithione adduct comprises from about 1 to about 40% by weight, based on the total weight of said antifouling agent.

30. The coating composition of claim 25 wherein said antifouling composition comprises from about 2 to about 75% by weight of said composition.

31. A method of reducing or inhibiting the growth of hard and soft organisms on a surface which comprises contacting the surface with coating composition and containing antifouling composition comprising particles of copper pyrithione and a copper containing compound, or oxide or hydroxide thereof.

32. A method of making an antifouling composition comprising combining copper pyrithione with cuprous oxide in the presence of a surfactant, said antifouling composition being effective against hard-fouling and soft-fouling organisms.

33. A method of forming the composition of claim 1 which comprises reacting relatively water insoluble copper powder or a copper salt with a relatively more water soluble pyrithione compound in a transchelation reaction.

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34. The method of claim 33 wherein the process is conducted in water by contacting a slurry of the "insoluble" copper source with a solution of the "soluble" pyrithione source, whereupon an insoluble copper pyrithione coating is formed on the slurried "insoluble" copper source in a manner that is controllable and can be formed in a fashion that is ideal for releasing biocidal quantities of both soft and hard fouling agents to control fouling. These engineered particles are filtered from the water media from which they are formed, dried, and are suitable for reformulation in a variety of media such as paints, powder coatings, dipping solution, polymers and plastics.

35. The composition of claim 1 wherein the core material is copper I oxide and the coating material is copper II pyrithione.

36. The composition of claim 35 wherein the weight ratio of copper oxide to copper pyrithione is from 5:1 to 15:1 and the coating diameter is about 1% of the idealized spherical particle.

37. The composition of claim 36 wherein the weight ratio of copper oxide to copper pyrithione is about 10:1 and the diameter of the coating material is about one percent of the diameter of each of said composite particle as calculated for said composite particles being idealized spheres.

38. A biocidal composition comprising composite particles containing a shell and a core, said core comprising a filler or a biocide and said shell comprising a pyrithione adduct derived from a portion of the core metal.

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39. A shampoo, soap skin care medicament, or combination thereof, comprising a surfactant and composite particles, each said composite particle containing a shell and a core, said core comprising a metal or a metal-containing compound comprising a moiety selected from the group consisting of zinc, copper, bismuth, silver, iron, titanium, aluminum, zirconium and combinations thereof, and said shell comprising a pyrithione salt comprising pyrithione and said moiety.

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